

## ORGANIC OXYGEN CONTENTS OF ARGONNE PREMIUM COAL SAMPLES

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### ABSTRACT

The organic oxygen content has been determined for the Argonne premium coal samples through fast neutron activation analysis (FNAA) of the dry original coal and low temperature ash (LTA). This is compared with the oxygen-by-difference method using elemental analysis and high temperature ash corrected by the Parr Formula. The total organic oxygen content is compared with oxygen functional group contents as determined by chemical and flash pyrolysis techniques.

### INTRODUCTION

The organic oxygen components of coal are important in determining coal structure and reactivity in coal liquefaction and other processes (1). Coal contains substantial amounts of chemically bound oxygen in the organic components in addition to the oxygen associated with mineral matter in coal. The total oxygen content decreases with the rank of the coal (2). The conventional ASTM method (3) used to estimate the organic oxygen content of coal is to subtract from 100 the sum of the percentages of carbon, hydrogen, nitrogen, sulfur, and high temperature ash. All errors in these determinations and errors due to large weight changes in the coal mineral matter in the ASTM high temperature ash method are included in the oxygen-by-difference estimate. This can be corrected to some degree by the modified Parr Formula (4), but the result is only an estimate.

Fast neutron activation analysis (FNAA) has been used to determine organic oxygen of coal directly by several workers (5,6,7). Low temperature ashing instead of ASTM high temperature ash method has been used with fast neutron activation analysis of the ash and the dried coal for the determination of organic oxygen (5,6). Mahajan (7) and others have reported that, during low temperature ashing of coals, mineral matter present in coal undergoes minimal change in composition. Organic oxygen is calculated from the following difference of FNAA determinations of total dry coal oxygen and oxygen in low temperature ash.

$$\% O_{\text{organic}} = \% O_{\text{total}} - \% O_{\text{LTA}} \times g \text{ LTA/g coal}$$

The problems involved in determining the organic oxygen content of coal were discussed in detail by Given and Yarzab (8).

Oxygen structures in coal give off water, carbon monoxide or carbon dioxide on pyrolysis, and the temperatures at which these are evolved depend on the functional groups. Pyrolysis together with NMR and other analytical methods may allow us to identify the particular oxygen functional groups in the coal, and correlate this with process studies.

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There is chemical evidence for the presence of hydroxyl, carbonyl, carboxyl, and methoxy groups in low-rank coals, and for hydroxyl and carbonyl groups in higher rank coals (9, 10). However a certain fraction of the oxygen is not detected by standard chemical analyses and is usually considered to be ether oxygen. It has been speculated that coal liquefaction consists at least in part in the cleavage of ether linkages between aromatic ring clusters (11, 12), leaving free radical ends which are capped by hydrogen transfer from coal or a donor solvent. Cleavage of ether groups might be expected to give more phenolic groups (13). The principal evidence for this is the presence of more phenolic groups after liquefaction than were present in the original coal (12, 14). However, the presence and type of ether groups in coal and the role of oxygen functionalities in coal liquefaction is still obscure (1).

It is to try to provide more information on the oxygen functional groups distribution and organic oxygen species in coal and their roles in coal processes that this work was undertaken. The research described will be an important step toward understanding the chemistry of the coal pyrolysis process. To the extent that it is successful in developing an understanding of coal structure it will also assist in developing an understanding of coal liquefaction and other coal conversion processes.

## EXPERIMENTAL

### Coals Studied

The eight coals from the Argonne premium coal sample program were studied (see Table I).

### Low Temperature Ashing

The low temperature ashier (LFE Corp., LTA-302) was operated at around 75-100 W depending on fluctuations in the unit while running. The oxygen flow rate was kept at 100 cc/min. All the samples (approximately 0.2 g) were ashed after being ground under nitrogen for one hour with a mortar and pestle. The samples in the boat were stirred to expose fresh surface for oxidation approximately every 5 hours. Ashing was continued until constant weight of the sample was obtained. All of the low temperature ash samples were sealed in air tight vials in the nitrogen atmosphere of a glove box. In the case of Wyodak and Beulah samples the low temperature ash was measured on both the original and acid forms.

### Chemical Methods

The chemical methods of Blom and Schafer (9, 10) were used for analysis of the oxygen functional groups in coal such as carboxyl, hydroxyl, and carbonyl. Ethers (internal and external) were estimated by difference. Kjeldahl nitrogen runs as part of the carbonyl determination were run by Micro Analysis Inc.

### Pyrolysis Method

The pyrolysis experiments were conducted on the Beulah-Zap and Wyodak samples at 625-930°C with 74-105  $\mu$ m fractions in a continuous fluidized sand bed pyrolyzer (described in detail in reference 15). The coals used were ground in a SPEX mill or mortar and pestle in a nitrogen atmosphere, sieved, and then vacuum dried at 104-107°C for approximately 20 hours. The coal particles were entrained into a nitrogen stream in the coal feeder and carried over into the fluidized sand bed at various flash pyrolysis temperatures.

The coal feeder was suspended from a Mettler balance and the change in its weight with time was monitored by a Linseis recorder. Coal was fed at uniform rates of 0.03-0.1 grams/min and approximately 1-2 grams total are fed. Upon entering the pyrolyzer, the coal was rapidly heated to the bed temperature at a rate of approximately  $10^4$  °C/sec and residence time (assuming full utilization of the expanded fluidized sand bed) was about 0.5 sec. Thermocouple wells in the reactor allow close monitoring of the temperature in the reactor bed and in the region above it. The pyrolysis products exit the pyrolyzer to a set of three cold traps. A side stream after the first trap can be vented to a Panametrics hygrometer for measurement of water content. The gases were collected and analyzed for CO and CO<sub>2</sub> in a Perkin-Elmer Sigma 1B gas chromatograph. The tars were collected in Soxhlet thimbles for later recovery by Soxhlet extraction with methylene chloride and subsequent analysis in an HP5880A gas chromatograph/mass spectrometer.

## RESULTS AND DISCUSSION

**Organic Oxygen Content:** We have run eight Argonne National Laboratory (ANL) premium coal samples in the low temperature asher. The remaining ash, after the sample reached constant weight, was analyzed by Radioanalytical Services of the University of Kentucky for determination of percent oxygen through fast neutron activation. This value was subtracted from the total oxygen content, which was determined in the same manner on the dried coal itself, to give the percent organic oxygen for each sample of coal. Oxygen values reported by FNAA are for at least three replicate analyses of the same sample. The oxygen contents of eight coals and their low temperature ashes are shown in Table 1. A comparison of % low temperature ash of the samples between our experiments and ANL data (16) are generally in close agreement, except for the Beulah-Zap and Wyodak samples which are somewhat higher in this study. The reason for this difference is not apparent. The organic oxygen contents of the dried coals determined by FNAA method are compared in Table 2 with those determined by oxygen-by-difference using elemental analysis and high temperature ash corrected by the Parr Formula. These two values are generally in agreement. Table 3 shows the elemental analysis of samples (16) by direct determination including the contents of low temperature ashes and the total organic oxygen determined by FNAA method. It will be noted that the total of these values are approximate 100 %, except for the Illinois #6 coal which is somewhat high. The reason for this is being investigated.

Low-rank coals contain the large concentration of exchangeable metal ions associated with the carboxyl groups. In the case of Wyodak and Beulah-Zap samples, the comparison of % low temperature ash of the original and acid forms show significant concentrations of associated metal ions, as shown in Table 4.

**Chemical Methods:** The percent oxygen as carboxyl, hydroxyl, carbonyl, and ether (by difference) in each sample is shown in Table 5. Carboxylic groups are found in considerable concentration in the low-rank coals. The percent oxygen in carboxyl groups decreases with increasing rank and approaches zero for coals of higher rank. The percent oxygen as hydroxyl and carbonyl show similar trend with increasing rank, but carbonyl shows greater variability. There is significant amounts of ether oxygen (by difference) in all samples. Illinois #6 coal, however, seems to be somewhat lower in ether oxygen than might be expected for its rank.

**Flash Pyrolysis:** The pyrolysis of coal over a range of controlled conditions offers a possible unexploited and independent approach to studying the oxygen species in coal. The structural interpretations of pyrolysis data of coal sample are compared to total organic oxygen contents determined by FNAA and oxygen functional group contents such

as % carboxyl, % hydroxyl, % carbonyl, and % ether (by difference) by chemical methods.

The corresponding oxygen yields of Wyodak subbituminous as a function of pyrolysis temperature are shown in Figure 1. The main oxygen-containing products of the decomposition of oxygen groups of the sample are  $H_2O$ ,  $CO_2$ , and  $CO$ . Some water is adsorbed in coal and some may appear through decomposition of chemical structures. Carboxyl content as determined by  $CO_2$  evolution agrees closely with chemical analysis indicating that carboxyl groups pyrolyze quantitatively to  $CO_2$  (17). Water and  $CO_2$  evolution occurs below 700 °C.

$CO$  is a major gaseous product of coal pyrolysis and oxygen yield as  $CO$  continues increasing with temperature up to 930 °C. More experimental work is need to confirm the carbon monoxide emissions at temperatures in the range of 950-1000 °C. Based on model compounds studied, hydroxyl and ether groups appear to evolve mainly carbon monoxide and possibly water. Very preliminary work by one of the writers (15) at temperatures in the range of 600-1000 °C tend to confirm those observations and suggest that in our system these carbon oxide emissions may be complete and reasonably quantitative by 950-1000 °C.

Total oxygen yield from oxygen-containing groups increased with temperature. The total organic oxygen contents of the sample determined by flash pyrolysis technique and fast neutron activation analysis are in fairly close agreement.

## CONCLUSIONS

The conclusions of this work are as follows

1. The organic oxygen contents of the dried coals determined both by FNAA method and by oxygen-by-difference using the modified Parr Formula on high temperature ash are generally in agreement.
2. The percent carboxyl, hydroxyl, and carbonyl groups of samples decrease with increasing rank. Ethers represent a significant fraction of the organic oxygen in the Argonne coals.
3. Temperatures approaching 1000 °C are required to pyrolyze all the oxygen groups in coal.
4. Carboxyl groups in coal pyrolyze quantitatively to  $CO_2$  below 700 °C.
5. A substantial proportion of the mineral matter in low-rank coals is associated with the carboxyl groups.

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Table 1. Organic Oxygen Contents of Argonne Premium Coal Samples (dry, wt %) by Fast Neutron Activation Analysis

Coal	Beulah-Zap	Wyodak-Anderson	Illinois # 6	Blind Canyon	Pittsburgh # 8	Lewiston-Stockton	Upper Freeport	Pocahontas # 3
Rank C(dmmf)	Lig. 74.05	Subb. 76.04	HVB. 80.73	HVB. 81.32	HVB. 84.95	HVB. 85.47	MVB. 88.08	LVB. 91.81
LTA by ANL	8.7	8.7	18.1	5.3	10.9	21.6	15.3	5.5
LTA <sup>a</sup>	11.88	11.51	19.77	5.7	10.05	21.9	15.7	5.8
O <sub>LTA</sub> <sup>b</sup>	51.3	55.5	37.9	48.0	41.4	49.1	38.4	45.4
O <sub>T</sub> <sup>c</sup>	23.3	20.7	14.9	12.5	10.9	16.5	8.93	4.22
O <sub>org</sub> <sup>d</sup>	17.2	14.31	7.41	9.76	6.74	5.75	2.90	1.59

<sup>a</sup> Low temperature ash in this study

<sup>b</sup> Oxygen content of low temperature ash by FNAA

<sup>c</sup> Total oxygen content of coal by FNAA

<sup>d</sup> Organic oxygen content of coal by  $\% O_{\text{organic}} = \% O_{\text{total}} - \% O_{\text{LTA}} \times g \text{ LTA/g coal}$

Table 2. Comparison of Organic Oxygen Contents of Argonne Premium Coal Samples (dry, wt %) by Fast Neutron Activation Analysis and Oxygen-by-Difference Methods

Coal	Beulah-Zap	Wyodak-Anderson	Illinois # 6	Blind Canyon	Pittsburgh # 8	Lewiston-Stockton	Upper Freeport	Pocahontas # 3
Rank C(dmmf)	Lig. 74.05	Subb. 76.04	HVB. 80.73	HVB. 81.32	HVB. 84.95	HVB. 85.47	MVB. 88.08	LVB. 91.81
ANL <sup>a</sup> O <sub>org</sub> <sup>b</sup>	17.01	15.21	8.21	10.29	6.13	5.17	3.98	1.57
Exp. <sup>c</sup> O <sub>org</sub> <sup>d</sup>	17.21	14.31	7.41	9.76	6.74	5.75	2.90	1.59

<sup>a</sup> Argonne National Laboratory

<sup>b</sup> Organic oxygen content of coal by difference using elemental analysis and high temperature ash % corrected by Parr Formula

<sup>c</sup> Our experimental data by FNAA

<sup>d</sup> Organic oxygen content of coal by  $\% O_{\text{organic}} = \% O_{\text{total}} - \% O_{\text{LTA}} \times g \text{ LTA/g coal}$

Table 3. Elemental Analysis by Direct Determination of Argonne  
Premium Coal Samples (dry, wt %)

Coal	Beulah- Zap	Wyodak- Anderson	Illinois # 6	Blind Canyon	Pittsburgh # 8	Lewiston- Stockton	Upper Freeport	Pocahontas # 3
Rank C(dmmf)	Lig. 74.05	Subb. 76.04	HVB. 80.73	HVB. 81.32	HVB. 84.95	HVB. 85.47	MVB. 88.08	LVB. 91.81
Ca	65.85	68.43	65.65	76.89	75.50	66.20	74.23	86.71
Ha	4.36	4.88	4.23	5.49	4.83	4.21	4.08	4.23
Na	1.04	1.02	1.16	1.50	1.49	1.25	1.35	1.27
Si	0.80	0.63	4.83	0.62	2.19	0.71	2.32	0.66
Cl	0.04	0.03	0.05	0.03	0.11	0.10	0.00	0.19
Fa	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O <sub>org</sub> <sup>b</sup>	17.21	14.31	7.41	9.76	6.74	5.75	2.90	1.59
LTA <sup>c</sup>	11.88	11.51	19.77	5.7	10.05	21.9	15.7	5.8
Total	101.18	100.81	103.10	99.99	100.91	100.12	100.58	100.45

<sup>a</sup> Data from ANL user handbook

<sup>b</sup> Organic oxygen content of coal by  $\% O_{\text{organic}} = \% O_{\text{total}} - \% O_{\text{LTA}} \times \text{g LTA/g coal}$

<sup>c</sup> Low temperature ash in this study

Table 4. Metal Ions Associated with Low-Rank Coals

Coal	Beulah-Zap (wt %)	Wyodak-Anderson (wt %)
Low Temperature Ash on Raw Coal	11.88	11.51
Low Temperature Ash on Acid Form	2.87	5.7
Associated Metal Ions	9.01	5.81

Table 5. Determination of Organic Oxygen Contents by Chemical and Pyrolytic Analyses of Argonne Premium Coal Samples (dry, wt. %)

Coal	Beulah- Zap	Wyodak- Anderson	Illinois # 6	Blind Canyon	Pittsburgh # 8	Lewiston- Stockton	Upper Freeport	Pocahontas # 3
Rank C(dmmf)	Lig. 74.05	Subb. 76.04	HVB. 80.73	HVB. 81.32	HVB. 84.95	HVB. 85.47	MVB. 88.08	LVB. 91.81
Total Organic O by FNAA (1)	17.21	14.31	7.41	9.76	6.74	5.75	2.90	1.59
% O as CO <sub>2</sub> H by Chemical Method (2)	3.81	3.33	0.23	0.23	0.16	0.20	0.14	0.05
% O as CO <sub>2</sub> H by Pyrolysis Method	3.94	3.14						
% O as OH by Chemical Method (3)	9.16	7.68	5.68	5.22	4.32	2.70	1.96	0.98
% O as C=O by Chemical Method (4)	1.96	0.74	0.93	0.63	0.18	0.18	0.44	0.32
% O as Ether by Difference (1) - (2) - (3) - (4)	2.28	2.56	0.57	3.68	2.08	2.67	0.36	0.24

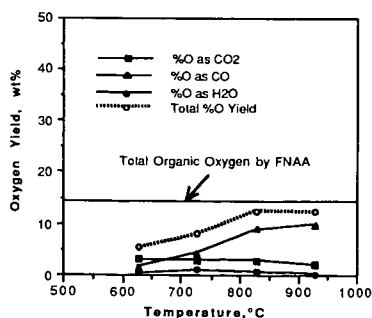


Figure 1. Oxygen Yield from Pyrolysis of Wyodak Subbituminous Coal in Fluidized Bed Pyrolyzer